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THE HEAT CAPACITY OF ELECTRO-POSITIVE METALS AND THE THERMAL ENERGY OF FREE ELECTRONS

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According to the classical principle known as the equipartition of energy the kinetic energy of every kind of atom which is capable of motion in any direction is the same, and the change in this kinetic energy for a change in temperature of one degree is $3R/2$ calories per gram atom. If in a solid substance each atom instead of moving freely vibrates about a more or less fixed position according to the laws of a simple oscillator, it will possess on the average a potential energy equal to its kinetic energy, and, if we consider the simple case in which the volume is kept constant the heat capacity per gram atom should be equal to $3R$, or 5.97 calories per degree.

According to the empirical law of Dulong and Petit, the atomic heat capacity at constant pressure is the same for most solid elements and equal to a little over 6 calories per degree. Lewis¹ calculated by means of a thermodynamic equation the difference between C_p and C_v and found for a considerable number of elements that C_v is more nearly constant and that its average value at 20°C., when a few elements of low atomic weight are omitted, is 5.9, which is almost identical with the theoretical value.

Much recent work, both experimental and theoretical, has shown that the earlier formulation of the equipartition law can no longer be considered as universally valid but rather as the expression of a limiting law which approaches complete validity the higher the temperature, the heavier the atom and the weaker the constraints operating upon the atom.² Every factor which causes a deviation from the equipartition law leads to a smaller specific heat than the one calculated by that principle. If therefore we find for any substance a value of C_v greater than $3R$ per gram atom we are led immediately to consider the possibility that in addition to the atoms other particles, either inside or outside of the atoms, are acquiring thermal energy.³

In the calculations of Lewis to which we have referred the value of C_v was found to be 6.4 for sodium and 6.5 for potassium, but the difference between these values and the theoretical values might at that time have been ascribed to experimental error. More recently Dewar⁴ has determined the mean atomic heats of a large number of elements between the boiling points of hydrogen and nitrogen. He found that at these low temperatures, where for most elements the atomic heat is only a small fraction of $3R$, that of cesium is 6.3. This is the value of C_p , but it seems likely that at such a low temperature the difference between C_p and C_v is very small even for an element like cesium. These facts led us to suspect that an abnormally high value of the atomic heat capacity might be a characteristic property of highly electro-positive metals. We were therefore interested to find that the experiments of Nernst and Schwes⁵ on the specific heat of magnesium showed for this metal a change of heat capacity with the temperature which at low temperatures corresponds with that obtained for other monatomic elements,⁶ but which at higher temperatures appears abnormally large.

In order to test the supposition that all electro-positive metals would exhibit this kind of abnormality we have determined over a wide range of temperature the specific heats of two metals of the first group, sodium and potassium, and of two metals of the second group, magnesium and calcium. The detailed measurements and the experimental method will be described shortly in the *Journal of the American Chemical Society*. Here we shall give only the general results of the investigation.

Before discussing the heat capacities found for the four metals it will be well to review briefly previous work on the heat capacities of other typical metals. Of these aluminum, copper, zinc, silver, mercury (solid), thallium and lead have been fully investigated over a wide range of temperature. For all of these metals C_v has been found to be the same function of T/θ , where T is the absolute temperature and θ is the temperature at which C_v is equal to $3R/2$. In other words, if we follow the procedure of Lewis and Gibson and plot C_v against $\log (T/\theta)$ the individual values of C_v for all these metals fall upon the same curve, which they speak of as the regular curve, or the curve of Class I. This may be expressed in still another way by the statement that if the values of C_v as ordinates are plotted against the values of $\log T$ as abscissae the curves for the several elements may be made to coincide by horizontal displacement.

The form of the regular curve is shown by the continuous curve of figure 1, where C_v is plotted against the common logarithm of the temperature, and the individual points are those found for magnesium. The five lowest points are taken from the measurements of Nernst and Schwes⁷ and the remainder represent our own measurements. It is evident that at low temperatures the specific heat curve for magnesium coincides with the regular curve, but that at higher temperatures the specific heat rises more rapidly than in the case of any of the other metals to which we have referred.

That this same phenomenon is exhibited by potassium, sodium and calcium is shown in figure 2, where the regular curve which would fit the experimental points at lower temperatures is drawn as a continuous curve and the individual points represent our experimental determinations of the heat capacity. In each of these cases the heat capacity rises well above the theoretical value $3R$.

The deviation from the regular curve at any one temperature is greater for calcium than for magnesium and greater for potassium than for sodium. We may therefore predict that this phenomenon is more marked the more electro-positive the metal, but that it will be found for every substance at high temperatures. According to modern theories of atomic structure the atom can

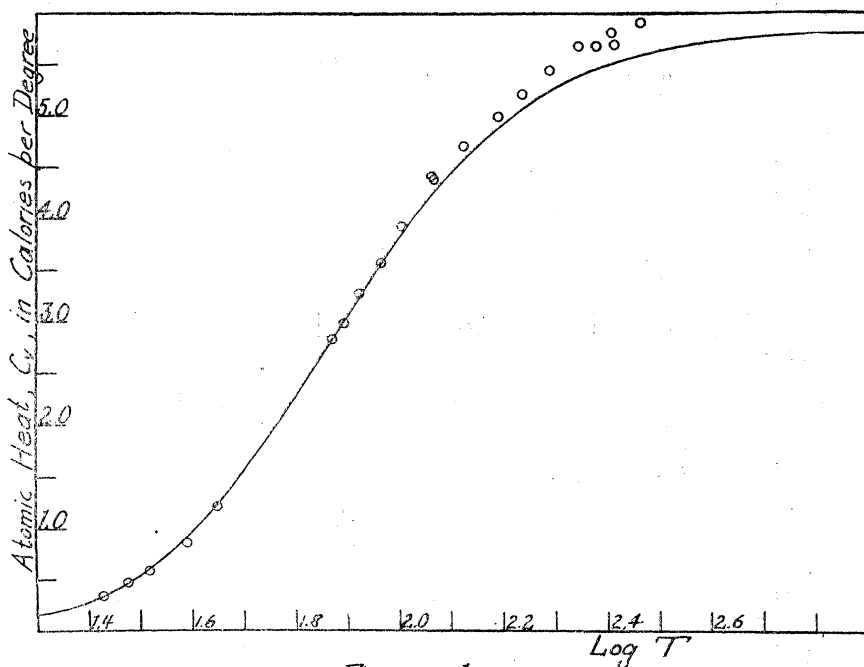
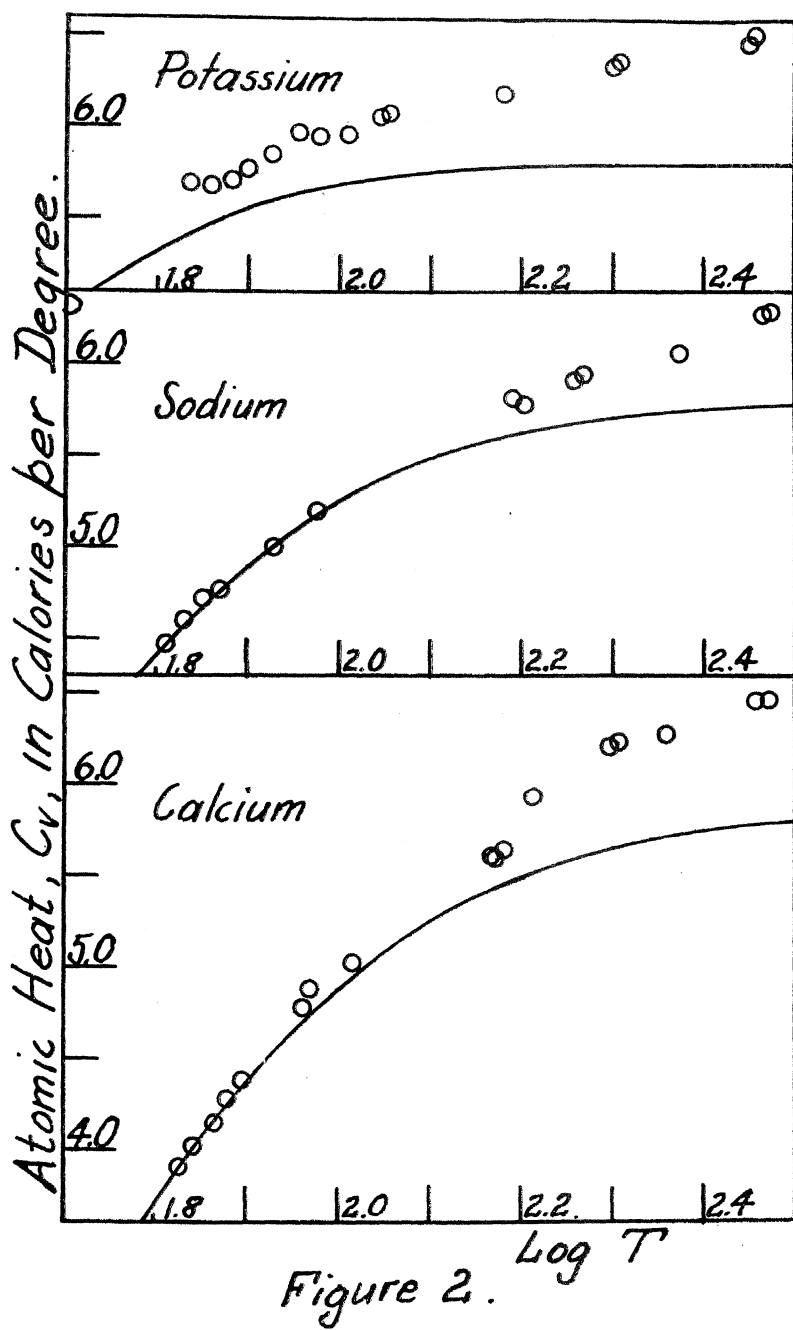


Figure 1.

no longer be regarded as the ultimate unit of matter. Besides the atomic nucleus there are electrons, and all of these particles, if capable in any degree of independent motion, should according to the earlier theory of the equipartition of energy, acquire their full share of thermal energy. If, however, we admit that at a given temperature deviations from the equipartition principle occur to an extent which is greater the lighter the particle and the more rigid the constraint which holds it to a fixed position, then it follows that at a temperature at which other particles are gaining thermal energy approximately according to the equipartition law, the electron which is by far the lightest of all particles, will acquire very little energy unless bound by very weak con-



straints. The optical properties of most substances show their electrons to be held rather rigidly, but many of the properties of metals, and especially of metals pronouncedly electro-positive in character, indicate a high degree of electronic freedom.

It is therefore our belief that in the metals under consideration the difference between the heat capacity observed and that calculated from the regular curve, which fits the experimental curve at low temperatures, may be regarded as representing the actual heat capacity of their more loosely bound electrons. Whether these electrons are 'free' in the sense that each electron occupies a position symmetrical with respect to two or more atoms, or whether they remain attached to individual atoms, we should expect them to add to the heat capacity of the substance, provided that they are held by sufficiently weak constraints.

We have thus an entirely new method of investigating the freedom of electrons in a metal, and it is to be hoped that when further quantitative data are available a comparison of the results obtained by this method with those obtained through a study of the photo-electric effect, or the Volta effect, will prove of interest.

¹ Lewis, *J. Amer. Chem. Soc., Easton, Pa.* **29**, 1907, (1165); *Zs. anorg. Chem., Hamburg*, **55**, 1907, (200).

² Lewis and Adams, *Physic. Rev., Ithaca, N. Y.*, (Ser. 2), **4**, 1914, (331).

³ Langmuir, *J. Amer. Chem. Soc., Easton, Pa.*, **38**, 1916, (2236), calls attention to the possibility that the atom in a solid may not be vibrating in simple harmonic motion and hence that the potential energy may not be equal to the kinetic energy, as has been assumed. However, if this were the case the potential energy would in all probability be less than the kinetic energy and not greater.

⁴ Dewar, *London, Proc. R. Soc., A*, **89**, 158, 1913, (158).

⁵ Nernst and Schwers, *Berlin Sitz. Ber. Ak. Wiss.*, 1914, (1), (255).

⁶ See Lewis and Gibson, *J. Amer. Chem. Soc., Easton, Pa.*, **39**, 1917, (2554).

⁷ The four highest points of Nernst and Schwers have been omitted since they appear to us to be erroneous.

THERMO-ELECTRIC DIAGRAMS ON THE P-V-PLANE

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Read before the Academy, November 21, 1917

About thirteen years ago I made an ill-directed and unfortunate attempt to analyze the electromotive force of a thermoelectric circuit, that is, to identify and explain the local e.m.f.'s which, taken together, give the e.m.f. of the circuit as a whole. I am now making a new attempt. I know that my present effort is more intelligently directed than the former one, and hope that it will prove to be more fortunate; but I do not claim for it finality.